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(56) References: BREK D., "Zeolitic molecular sieves". Published by "Mir", Moscow, 1976; pp. 324 -327.
Patent RU 2033963 C1, April 30, 1995,
RU 2146223 C1, March 10, 2000,
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SU 115564 A, May 15, 1985.

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(54) METHOD OF PREPARING GRANULAR FAUJASITE TYPE ZEOLITE WITHOUT BINDING MATERIALS

[Page 2:]

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(51) Int. Cl.[7] **C 01 B 39/20**

(12) DESCRIPTION OF INVENTION PERTAINING TO A RUSSIAN FEDERATION PATENT

(57)

The invention relates to the processing of natural clay materials, in particular for obtaining granulated synthetic zeolites without binders, for application as adsorbents and catalysts. The natural clay material is subjected to thermal activation and mixed with alumina-silica hydrogel with simultaneous introduction of amorphous silica into the reaction mixture, which is then granulated, dried and subjected to hydro-thermal crystallization in alkaline solution. In the quality of alkaline solution use is made of 40 - 60 g/l aqueous sodium hydroxide admixed with lithium hydroxide and in the presence of silicate or aluminate ion, depending on the SiO_2/Al_2O_3 mole ratio.

The crystallization is conducted at a weight ratio between clay material and lithium hydroxide of 100 : 0.1 - 0.5 at 85 - 100°C during 20 - 36 hours. The invention allows to shorten the time of crystallization. Three tables.

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(12) ABSTRACT OF INVENTION

(57) Abstract:

FIELD: processing of natural clay materials more particularly preparation of granular synthetic zeolites as adsorbents and catalysts. SUBSTANCE: natural clay material is thermally activated, mixed with alumosilicon hydrogel and amorphous silica is added to reaction mixture, mixture is granulated, dried and hydrothermal crystallization is carried out in alkaline solution which is sodium hydroxide having concentration of 40 - 60 g/l in admixture with lithium hydroxide and in the presence of silicate- or aluminate- ion depending on the SSS mole ratio. Crystallization is carried out at clay material to lithium hydroxide molar ratio of 100 : 0.1 - 0.5 at 85 - 100°C for 20 - 36 h. Invention makes it possible to shorten crystallization time. EFFECT: more efficient preparation method, 2 ex., 3 tbl.

The invention relates to the processing of natural clay materials, in particular aimed at obtaining granulated synthetic zeolites without binders, applicable in the quality of adsorbents.

Difficulties in manufacturing zeolites of NaX type without binders comprise the narrow range of crystallization which strongly overlaps with the crystallization ranges for zeolite of types A, Hydrosadolite and P, the long time of crystallization, and the high concentrations of the crystallization solutions, causing a tendency for recrystallization into zeolite of NaP type which crystallizes in the same range of compositions and is thermo dynamically the more stable phase.

A method is known for the obtaining of synthetic zeolite of NaX type by mixing meta-kaolin with alumina-silica hydrogel and amorphous silicon dioxide, followed by forming, drying of the granules and hydrothermal crystallization during 68 hours in an alkaline solution of 60 g/l NaOH concentration in the presence of ions of sodium aluminate [1].

Closest to the present invention is a method of preparation of granulated zeolite of faujasite type from activated natural clay material, according to which the zeolite is obtained by mixing the activated material with alumina-silica hydrogel and silicon oxide or aluminum hydroxide, forming, drying of the granules, and hydrothermal crystallization during 40 h in an alkaline solution of 120 -140 g/l NaOH concentration [2].

A drawback of this method is the alkalinity of the crystallization solution with as a consequence large amounts of alkaline industrial effluent, making for a tense ecological situation at the manufacturing site or, if the effluent is to be recycled, considerable material and energy expenditure.

The aim of the proposed technical solution consists in improvement of the ecological environment, shortening of the crystallization time, and savings of material and energy.

This aim is achieved by homogenizing the natural clay material, having been thermally activated, with alumina-silica hydrogel and amorphous silica or aluminum hydroxide, followed by granulation, drying, and crystallization in a sodium hydroxide solution of 40 - 60 g/l concentration in the presence of silicate or aluminate ion depending on the SiO_2/Al_2O_3 mole ratio, and with lithium hydroxide as an additive in 0.1 - 0.5 weight % amount referred to the clay material.

The crystallization is conducted at 85 - 100°C for 20 - 36 hours, depending on the sodium hydroxide concentration in the crystallization solution, the amount of additive, and the size of the granules.

The essence of the proposed technical solution consists in the fact that the addition of lithium hydroxide to the alkaline solution allows to create, during the crystallization in the hydrothermal system, the optimal conditions inside the granules for crystallization of faujasite-NaX. The lithium ions, of considerably smaller diameter than sodium ions, penetrate more readily into the pores, drawing the hydratation mantles along, whose water in its turn guides sodium ions along.

Thus the addition of lithium hydroxide to the crystallization solution optimizes the water-to-solids and water-to-alkali ratios inside the granules, and this, together with the chemical composition which is in the optimal range for the crystallization, enables to obtain an NaX zeolite of high phase purity, as well as shifting the chemical equilibrium towards

creation of target product, thereby allowing to shorten the time of crystallization and, without increasing the volume of crystallization solution, to reduce its concentration two- to threefold compared to the prior art.

Pertinent parameters and characteristics of the raw materials are listed in Tables 1 and 2 for purposes of comparison.

The essence of the proposed method is substantiated by the following example.

Example 1. This example demonstrates the feasibility of obtaining zeolite of type X from kaolin, being the clay material most widely employed technologically.

The raw kaolin is subjected to thermal treatment at 700 - 750°C during 3 - 6 hours. Of the thus activated kaolin, 1000 kg are mixed, in a mixer for granular materials, with 186.5 kg of amorphous silica for 30 - 40 minutes. The obtained 1186.5 kg of dry mixture is homogenized with 1323 l of an alkaline alumina-silica hydrogel obtained by mixing 900 l of sodium silicate [solution] with 424 l of sodium aluminate [solution]. In the sodium silicate solution the concentration of silicon dioxide was 170 g/l, and that of sodium oxide was 62 g/l. In the sodium aluminate solution the concentration of aluminum oxide was 213 g/l, and that of sodium oxide was 310 g/l.

The mass is blended for 50 minutes in a homogenizer for pasty materials, and is then granulated.

After drying, the granules, in 1606 kg weight, are charged into a crystallizer containing a crystallization solution.

The crystallization solution is the result of the mixing of 5865 l water, 1038 l of sodium hydroxide [solution] of 266 g/l NaOH concentration, 214 l of sodium silicate solution and 41 kg of lithium monohydrate *[sic]*. The obtained reaction mass is left to crystallize at 85°C for 36 hours.

The parameters of the zeolite obtained in this example are given in Table 3.

Example 2. This example demonstrates the feasibility of preparing zeolite-X from bentonite clay.

In a mixer for granular materials, 1000 kg of clay is mixed with 0.850 kg of aluminum sulfate for 40 minutes, and thereafter with 0.500 kg of caustic soda for 20 minutes.

Into this mass is blended 177.8 kg of aluminum hydroxide. The resulting mass is treated with steam at 170°C for 50 minutes.

After the hot-steam treatment the mass is subjected to thermal activation (calcination) at 720°C for 3 hours.

The obtained 1116.5 kg of mixture is blended, in a homogenizer for pasty materials, with 702 l of an alkaline alumina-silica hydrogel obtained by mixing 454 l of sodium silicate [solution] with 247.9 l of sodium aluminate solution. In the sodium silicate solution the concentration of silicon dioxide was 270 g/l, and the sodium oxide concentration was 93 g/l.

In the sodium aluminate solution the concentration of aluminum oxide was 280 g/l, and that of sodium oxide, 263.5 g/l. The mass is blended for 50 minutes and is then made into granules.

Thus the introduction of lithium hydroxide into the crystallization solution shortens the time of crystallization of NaX zeolite by a factor of 2, and allows to reduce the concentration of the solution, thereby reducing the amount of industrial effluent, improving the ecological situation at the production site, and reducing the consumption of materials and energy.

The proposed method has a great potential of implementation at the industrial level, as its crystallization times as well as the volumes and concentrations of industrial effluent are acceptable for a technological process.

Sources of information:

1. Russian Federation Patent Application No. 97104855, Int. Cl. 6 C 01 B 33/34, September 27, 1998.

2. Russian Federation Patent No. 2033966, December 12, 1992, Int. Cl. 6 C 01 B 39/20, bulletin No. 12 - April 30, 1995 (prior art).

Scope of patent claim: A method of preparation of granulated zeolite of type NaX without binders, on the basis of a clay material, comprising homogeneous mixing of the activated clay material with alumina-silica hydrogel and amorphous silicon dioxide or aluminum hydroxide, followed by	granulation, drying, and hydrothermal crystallization in alkaline solution, characterized in that the alkaline solution is a sodium hydroxide solution of 40 - 60 g/l concentration containing silicate or aluminate ions and furthermore lithium hydroxide in 0.1 - 0.5 weight % amount referred to the clay material.

Table 1

Parameters of crystallization

Name of starting material	Chemical composition of granules in mole ratios			Composition of crystallization solution, g/l				Time of crystallization, hours	Serial no.
	Na_2O/Al_2O_3		SiO_2/Al_2O_3	Na_2O	SiO_2	Al_2O_3	Li_2O		
Bentonite	0.36	3.25	105	-	5	-		40	1
			46.5	-	5	1.5		20	2
Kaolinite	0.48	2.9	46.5	5	-	-		68	3
			46.5	5	-	1.5		20	4
			31.0	5	-	1.5		36	5

Table 2

Characteristics of starting materials

Name of clay material	Chemical composition of clay material, %				
	Na_2O	Al_2O_3	SiO_2	CaO	Molar ratio SiO_2/Al_2O_3
Bentonite	< 0.1	20.37	57.05	1.31	4.76
Kaolinite	< 0.1	36.01	46.7	1.25	2.2

Table 3

No.	Zeolite type by X-ray analysis data	Faujasite content, weight %	Volume by benzene vapors, weight *[sic]* %	Dynamic activity by steam, mg/cm³
1	NaX	90	20	138
2	NaX	92	21	144.9
3	NaX	75	18	124.2
4	NaX	88	20	138
5	NaX	88	20	138